GOVERNMENT OF INDIA, THE PATENT OFFICE
214/ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 143864 dated 4th May., 1976.
Application and Provisional Specification No. 16/MAS/1976 dated 24th January, 1976
Acceptance of the complete specification advertised on 18th february 1978.

Index at acceptance— 32 E [IX (1)]

International Classification— C 08 g 17/02.

1. PROCESS FOR THE PRODUCTION OF POLYOLS.

2. INDIAN SPACE RESEARCH ORGANISATION DEPARTMENT OF SPACE GOVERNMENT OF INDIA, F' BLOCK, CAUVERY BHAVAN, DISTRICT OFFICE ROAD, BANGALORE 560 009

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

The invention relates to the PRODUCTION OF POLYOLS.

12-hydroxy stearic acid (12-HSA) is subjected to self-condensation in an aromatic solvent media in presence of catalysts like aromatic sulfonic acid, till the desired degree of polymerisation is attained. The polymerised product is the polycondensate of 12-HSA or simply Poly (12-HSA). The extent of the reaction or the degree of polymerization can be monitored by the amount of water collected or by the drop in acid value. Suitable modifiers like glycol, glycerol and trimethylol propane are added at the stage when desired degree of polymerisation is achieved and the condensation reaction is continued till completion, to get polyols of desired molecular weight and functionality.

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Dated this Twenty third day of January 1976.

T.N. SESHAN IAS
Joint Secretary to Govt of India
Dept. of Space
Ex Member Secretary (Finance)
ISRO Council

143854

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

1. PROCESS FOR THE PRODUCTION OF POLYOLS.

2. INDIAN SPACE RESEARCH ORGANISATION DEPARTMENT OF SPACE GOVERNMENT OF INDIA, F' BLOCK, CAUVERY BHAVAN, DISTRICT OFFICE ROAD, BANGALORE 560 009.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

Polyols or hydroxyl terminated polymers are the precursors of urethane polymers. Most of the commercial polyols are of polyether or polyester type. However, the polyether types have so far found wider applications and larger demand as compared to polyester type polyols in the urethane industry. Naturally occurring ester type polyols, like castor oil, have also been found suitable for various commercial applications. Castor oil and its derivatives have been used as polyols in three different ways: (a) unmodified castor oil as basic polyol (b) its transesterified product, and (c) esters of its fatty acids. The ester type polyols mentioned above could not lead on to wide and bulk applications in the urethane industry, as any modification in chemical structures of the ester type polyols was aimed to meet only a specific end use.

There have previously been attempts to get polymers from fatty acids of castor oil for various applications. For example, according to US Patent No. 27,85,978 mixture of fatty acids of castor oil have been intramolecularly polymerised at 200° to 230°C in vacuum for 16 hours under nitrogen atmosphere and further the resulting estolides have been esterified with high molecular weight polyglycerol. These products have been reported to be useful in the preparation of water-in-oil emulsion and chocolate coating for ice-cream briquettes. Almost similar products have been produced in semi-liquid or pasty form as described in Dutch Patent No. 82,891 and they are used as stabilizers and emulsifying agents.

Ehrlich, A., M.K. Smith and T.C.Patton, (J.Am. Oil Chem. Soc.36, 149 (1959))have reported various ricinoleic acid and 12-hydroxy stearic acid polyols for urethane foams and elastomer applications. These polyols are low molecular weight monoesters of ricinoleic acid and 12-hydroxy stearic acid with various glycols, glycerol or pentaerythritol. Though the polyols thus prepared would have higher functionality and increased molecular weight to a limited degree, the concept of polymerising the fatty acids of castor oil and suitably modifying the same has not been cited. Low molecular weight monoesters of ricinoleic acid have also been reported by Baker Castor Oil Co., USA under the trade name of Polycin. [See Patton T.C., A.Ehrilich, and M.K.Smith, Rubber Age (N.Y) 86, 639 (1960)].

US Patent No. 30,40,917 describes the composition of engine lubricating oils, containing rust inhibitor in which polyethlyene glycol-bis(triricinoleate) with a total molecular weight 2,000 has been used.

According to German Patent No. 19,40,294(Cl,008f), a polyester of molecular weight 1700 was prepared by autocondensation of 12 hydroxy stearic acid condensed with glycidyl methylacrylate, to introduce unsaturation, and copolymerised with methyl methacrylate. These polymers have been found to increase the stability of non-aqueous polymer dispersions.

German Patent No. 20,32,297 describes a hydroxyl terminated polyester produced by reacting diol or triol with poly (ω -hydroxy capsoic acid) or poly (12 hydroxy stearic acid) and these polyesters are used as urethane adhesives for polyvinyl chloride. The preparation of the polyesters with terminal polyhydroxy groups starting from 12-hydroxy stearic acid and their use as film forming coatings are described in US Patent No. 37,41,941.

However, none of the above patents cover the concept that is covered in the present invention that provides for a range of polyols for a variety of applications. The present invention, which adopts a method involving the use of the esters of fatty acids of castor oil for production of polyols, can produce polyols of average molecular weights ranging from 1500-3200 and functionality in the range of 2 to 4 and of any desired nature of functionality (viz. primary or secondary hydroxyl group) so as to substitute polyether based polyols, which are petrochemical based.

In this specification, unless otherwise specified 12-hydroxy acid is referred as THSA.

According to this invention, a process for producing polyols comprises homopolymerising 12-hydroxy stearic acid (THSA) in an aromatic solvent to poly THSA, is presence of an acid catalyst, monitoring the degree of polymerisation by measuring the drop in acid value of the said homopolymer till the degree of polymerisation ranging 2 to 10 is achieved, treating the said poly THSA with polyalcohols such as herein described, so as to react completely with the residual carboxylic groups of the said poly THSA and recovering the polyol from the reaction mixture by known methods. For example the recovery of the polyol may be effected by distilling off the solvent.

As an acid catalyst, for the process of this invention, anhydrous para-toluene sulfonic acid therein referred to as PTSA may be used. The said catalyst is removed from the reaction product by percolating the cooled mixture through an ion-exchange resin.

As example of polyalcohols used for the process of this invention, may be mentioned glycols, glycerols, tri-methylolpropane and pentaerythritol.

The chemical reactions taking place in the two steps are given below:-

Step -1 - Hyomopolymerisation

$$n\ HO\left[\underset{\underset{CH_3}{|}}{\underset{(CH_2)_5}{\underset{|}{CH}}} -(CH_2)_{10} - \overset{O}{\overset{\|}{C}} - O\right] - H \xrightarrow{\text{ACID CATALYST}} HO\left[\underset{\underset{CH_3}{|}}{\underset{(CH_2)5}{\underset{|}{CH}}} -(CH_2)_{10} - \overset{O}{\overset{\|}{C}} - O\right]_n H$$

12 - hydroxy stearic acid (THSA) Poly (12 hydroxy stearic acid)

or

Poly - THSA

$+(n-1)\ H_2O$

Step-2 - Modification

$$\mathrm{HO}\left[\underset{\substack{|\\(CH_2)_5\\|\\CH_3}}{CH}-(CH_2)_{10}-\overset{\overset{\large O}{\|}}{C}-O\right]_n H + HO-(CH_2)_n-OH + H_n\left[O-\overset{\overset{\large O}{\|}}{C}-(CH_2)_{10}-\underset{\substack{|\\(CH_2)_5\\|\\CH_3}}{CH}\right]OH$$

Poly-THSA Glycol Poly-THSA

$$\Big\downarrow \text{Acid catalyst}$$

$$\mathrm{HO}\left[\underset{\substack{|\\(CH_2)_5\\|\\CH_3}}{CH}-(CH_2)_{10}-\overset{\overset{\large O}{\|}}{C}-O\right]_n(CH_2)_n\ {}_n\left[O-\overset{\overset{\large O}{\|}}{C}-(CH_2)_{10}-\underset{\substack{|\\(CH_2)_5\\|\\CH_3}}{CH}\right]OH + 2H_2O$$

Difunctional Polyol (Poly-diol)

In the present invention, water formed during condensation-polymerisation of 12-hydroxy stearic acid is removed continuously by azeotropic distillation using a solvent (either aliphatic, cyclic or aromatic hydrocarbon) as entraining agent. Bawn et.al. (Bawn, C.E.H., and Huglin M.B. (Uni.Liverpool Engl.), Polymer 3, 257-62 (1962)) found that degree of polymerisation (DP) in melt polymerisation of THSA at a given temperature is proportional to the concentration of catalyst p-toluene sulphonic acid (PTSA). At a given temperature and concentration of the catalyst, the degree of polymerisation (DP) is found to increase linearly with time. The departure from this phenomenon is found to occur only at higher temperatures (above 150°C). In the present invention, polymerisation reaction temperature has been kept under control with the use of suitable solvent as entrainer.

As a first step, THSA is dissolved in toluene or xylene (to get 20 to 80% solution). THSA is homopolymerised in solution in the presence of the catalyst PTSA (0.1 to 2% of THSA) to the desired level (DP 2 to 10). The degree of polymerisation is monitored by noting down the drop in acid value of the homopolymer (poly-THSA). At this stage, as a second step, a low molecular weight poly-alcohol such as glycol, glycerol, trimethylolpropane, pentaerythritol as modifier is added to the product of Step-1 so as to react completely with the carboxyl content of poly-THSA. The polymerisation is continued further till the residual carboxyl groups of poly-THSA are reacted completely to get the desired polyol. The reaction products of Step-2 are percolated through a column of suitable ion-exchange resin where the catalyst, PTSA, is held back after exchange in the column. The entrainer toluene (or xylene) is recovered by distillation, leaving liquid polyol behind.

The nature of the hydroxyl groups (such as primary or secondary) in the final product polyol, the molecular weight of the final product polyol and the number of hydroxyl groups required per molecule of polyol can be controlled in Step-2, as desired, by following the procedure given in the present invention.

The following examples illustrate the typical methods of preparation of different molecular weight polyols modified by diethylene glycol (for poly-diol 1600 to 2000, 2200 to 2600 and 2800 to 3200 molecular weights), 1,1,1-trimethylol-propane (for poly-triol of 2200 to 2600 molecular weight with primary and secondary hydroxyl groups), glycerol (for poly-triol of 2100 to 2700 molecular weights having only secondary hydroxyl groups), pentaerythritol (for polytetrol of 2000 to 2500 molecular weight).

Example-1 - Preparation of poly-diol of 2200 to 2600 molecular weight range.

The experiment was carried out in four stages a, b, c and d as described below:-

a) 300 g of THSA (minimum 98% purity), 225 ml of distilled commercial toluene and 3 g of anhydrous p-toluene sulphonic acid were charged into a three necked round bottomed (one litre) flask with an arrangement for heating to 120° to 130°C and continuous removal of water azeotropically (Dean and Stark trap). The reaction mixture was kept under agitation by a mercury seal stirrer, fitted to the flask. The water formed by condensation was continuously removed from the system till 13.3 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 30.3 mg KOH/g).

b) 13.25 g of freshly distilled diethylene glycol was added to the reaction product of (a) immediately after 13.3 g of water was collected. The reaction was further continued till an additional 4.5 g of water was collected and the acid value dropped to 2.3 mg KOH/g.

c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml. per hour

d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 265 g of poly-diol having the following properties:

1.	Hydroxyl value (mg KOH/g)	...	47.5
2.	Acid value (")	...	1.32
3.	Iodine value	...	1.07
4.	Viscosity at 30°C in cps	...	2100
5.	Specific gravity at 27°C	...	0.926
6.	Average molecular weight	...	2250

Example-2 - Preparation of poly-diol of 1600 to 2000 molecular weight range

a) The procedure followed was same as given in (a) of Example-1, except that the water formed by condensation was continuously removed from the system till 11.74 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 40.54 mg KOH/g).

b) 17.6 g of freshly distilled diethylene glycol was added to the reaction product of (a) immediately after 11.74 g of water was collected and the reaction was further carried out till an additional 6.45 g of water was collected and the acid value dropped to 2.25 mg KOH/g.

c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.

d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 259 g of poly-diol, having the following properties:

1.	Hydroxyl value (mg KOH/g)	...	71.0
2.	Acid value (")	...	0.89
3.	Iodine value	...	0.98
4.	Viscosity at 30°C in cps	...	2400
5.	Specific gravity at 27°C	...	0.929
6.	Average molecular weight	...	1690

Example-3 - Preparation of poly-diol of 2800 to 3200 molecular weight range

a) The procedure followed was same as given in (a) of Example-1, except that the water formed by condensation was continuously removed from the system till 14.32 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 23.83 mg KOH/g).

b) 10.28 g of freshly distilled diethylene glycol was added to the reaction product of (a) immediately after 14.32 g of water was collected and the reaction was further continued till an additional 3.74 g of water was collected and acid value dropped to 2.79 mg KOH/g.

c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.

d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 250 g of poly-diol having the following properties:-

1.	Hydroxyl value (mg KOH/g)	...	32.3
2.	Acid value (")	....	1.2
3.	Iodine value	...	1.8
4.	Viscosity at 30°C in Cps	...	2700
5.	Specific gravity at 27°C	...	0.920
6.	Average molecular weight	...	2820

Example-4 - Preparation of poly-triol of 2200 to 2600 molecular weight range with primary and secondary hydroxyl groups

a) The procedure followed was same as given in (a) of Example-1, except that the water formed by condensation was continuously removed from the system till 13.3 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 30.43 mg KOH/g).

b) 16.32 g of 1,1,1-trimethylol-propane (TMP: poly-THSA: 1:2) was added to reaction product of (a) after 13.3 g of water was collected, and after cooling down the reaction mix to facilitate the addition of the trimethylol-propane. The reaction was further continued till an additional 4.95 g of water was collected and acid value dropped to 2.15 mg KOH/g.

c) The reaction mixture was cooled to room temperature ans was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.

d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flastk and was distilled under reduced pressure to recover the toluene and 260 g of poly-triol having the following properties:

1.	Hydroxyl value (mg KOH/g) ...	63
2.	Acid value (") ...	0.5
3.	Iodine value ...	0.81
4.	Viscosity at 30°C in cps ...	2100
5.	Specific Gravity at 27°C ...	0.932
6.	Average molecular weight ...	2260

Example-5 - <u>Preparation of poly-triol of 2100 to 2700 molecular weight range with only secondary hydroxyl groups</u>

a) The procedures followed was same as given in (a) of Example -1, exvept that the water formed by condensation was continuously removed from the system till 13.41 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 29.97 mg KOH/g).

b) 11.2 g of glycerine (minimum purity) 99%) was added to the reaction product of (a) immediately after 13.41 g of water was collected and the reaction was further continuted till an additional 4.90 g of water was collected and acid value dropped to 3.05 mg KOH/g.

c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.

d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 255 g of poly-triol having the following properties:

1.	Hydroxyl value (mg KOH/g)	...	53.00
2.	Acid Value (")	...	3.0
3.	Iodine value	...	0.98
4.	Viscosity at 30°C in cps	...	1800
5.	Specific gravity at 27°C	...	0.925
6.	Average Molecular weight	...	2350

Example-6 - <u>Preparation of poly-tetrol of 2000 to 2500 molecular weight range</u>

a) The procedure followed was same as given in (a) of Example-1, except that 210 ml of xylene was taken in place of toluene and that the water formed by condensation was continuously remeved from the system till 13.42 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 30.15 mg KOH/g).

b) 17.82 g of pentaerythritol was added to the reaction product of (a) immediately after 13.42 g of water was collected and the reaction was further continued till an additional 4.95 g of water was collected and acid value dropped to 2,95 mg KOH/g.

c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of 1 litre. The percolation rate was maintained at 20 ml per hour.

d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the xylene and 263 g of poly-tetrol having the following properties:

1.	Hydroxyl value (mg KOH/g)	...	82
2.	Acid value (")	...	1.8
3.	Iodine value	...	2.4
4.	Viscosity at 30°C in cps	...	2050
5.	Specific gravity at 27°C	...	0.937
6.	Average molecular weight	...	2050

We claim:

1. A process for producing polyols comprising homopolymerising 12-hydroxy Stearic Acid in an aromatic solvent to poly- (12-hydroxy stearic acid) in presence of an acid catalyst, monitoring the degree of polymerisation by measuring the drop in acid value of the said homopolymer till the degree of polymerisation ranging from 2 to 10 is achieved, treating the said poly-(12-hydroxy stearic acid) with poly alcohols such as herein described, so as to react completely with the residual carboxylic group of the said poly-(12-hydroxy stearic acid), and recovering the polyols from the reaction mixture by known methods.

2. A process for producing polyols as claimed in claim 1, wherein the said catalyst is anhydrous para-toluene sulphonic acid.

3. A process for producing polyols as claimed in claim 1, wherein the acid catalyst is removed from the reaction product by percolating the cooled mixture through ion-exchange resin.

4. A process for producing polyols as claimed in claim 1, wherein the said poly alcohols are glycols, glycerols, strimethylol-propane and pentaerythritol.

5. A process for the production of polyols substantially as herein described with referance to the examples.

Dated this 4th day of May 1976.

Sd/-
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